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SHORT COMMUNICATIONS

Sulfuration of 5-Benzylidenehydantoins

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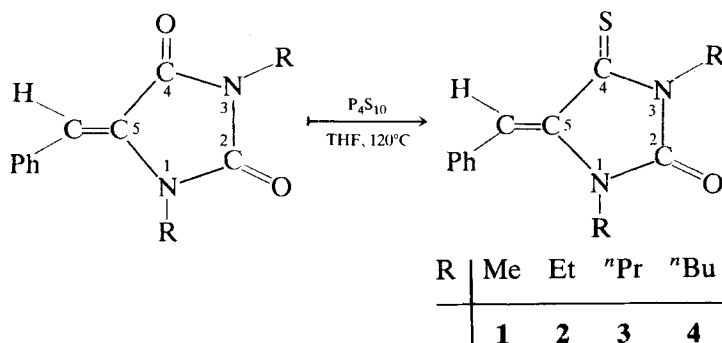
The thermal reaction of Z-5-benzylidene-1,3-dialkylhydantoins with tetraphosphorusdecasulfide leads to the Z-5-benzylidene-1,3-dialkyl-4-thiohydantoins **1-4**. The sulfuration occurs exclusively in position 4 of the hydantoin system; the corresponding E-isomers are not sulfurated at all.

INTRODUCTION

We recently found that alkylisocyanats react with phenylacetylen under catalytic conditions with C-N-coupling to give 5-benzylidenehydantoins.¹ A series of new Z- and E-dialkyl derivatives of this system became accessible by this reaction. We report here on the sulfuration of these heterocycles to the corresponding 5-benzylidene-4-thiohydantoins.

RESULTS AND DISCUSSION

The thermal reaction of Z-5-benzylidene-1,3-dialkylhydantoins with P_4S_{10} at 120°C yields the Z-5-benzylidene-1,3-dialkyl-4-thiohydantoins **1-4**. The sulfuration takes place exclusively in position 4 of the hydantoin ring; the formation of the 2,4-dithiohydantoin derivatives is not observed even at 200°C. This is surprising in view of fact that in [4.5]-spiroheterocycles with analogous CO-NR-sequence all CO groups can be successively converted into CS-groups;² however, it is in accordance with similar results for hydantoin.³ Contrary to the Z-derivatives the corresponding E-5-benzylidene-1,3-dialkylhydantoins cannot be sulfurated with P_4S_{10} .



The new thiohydantoin 1–4 are isolated by chromatographic methods and obtained as orange, air-stable compounds. The mass spectra show besides the molecular ion fragment ions originating from the loss of R- and RNCO-fragments. In the infrared spectra the expected $\nu(\text{C}=\text{O})$, $\omega(\text{C}=\text{C})$ and $\nu(\text{C}=\text{S})$ absorptions are observed. The ^1H -NMR-spectra exhibit the separated signals for the substituents at N(1) and N(3); the resonance of the olefinic proton coincides with the multiplet of the phenyl group. The assignment of the structure of 1–4 is based on the ^{13}C -NMR-spectra: Besides the signals caused by the substituents at N(1) and N(3) and the phenyl groups four resonances are found for the olefinic carbon at C(5), the exocyclic carbon atom, the carbonyl and the thiocarbonyl C-atoms. By comparison with the ^{13}C -NMR-spectra of the starting compounds it can be shown that the sulfuration has taken place in position 4: While the ^{13}C -signal of the nonconjugated carbonyl group C(2) at about δ 156 ppm is almost the same in starting material and product, the signal at about δ 164 ppm, due to the conjugated carbonyl C(4) of the starting material, is not observed for the product; but the signal of the thiocarbonyl at about δ 189 ppm appears instead.

The parent system of the 5-benzylidene-4-thiohydantoin is already known: the unsubstituted 5-benzylidene-4-thiohydantoin was obtained by condensation of 4-thiohydantoin with benzaldehyde; the configuration at the double-bond, however, is unclear.⁴

EXPERIMENTAL

General Data. The ^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR-spectra, reported in parts per million (δ) were obtained with a Jeol FX 90 Q spectrometer. IR spectra were recorded with a Perkin-Elmer 983 G spectrometer, mass spectra with a Varian MAT 312 spectrometer. Thin-layer-chromatography was performed with Merck Kieselgel TLC 60 GF₂₅₄. Starting materials were prepared as previously published.¹

Z-5-Benzylidene-1,3-dialkyl-4-thiohydantoin. General procedure. A suspension of Z-5-benzylidene-1,3-dialkylhydantoin (0.44 mmol) and P_4S_{10} (1.10 mmol) in 20 ml tetrahydrofuran is heated in a stirred autoclave to 120°C for 24 hours. After cooling the suspension is filtered over filter pulp. The residue is extracted with 20 ml CH_2Cl_2 and 20 ml diethylether; the extracts are combined with the filtrate and evaporated to dryness. The residue is taken into 5 ml CH_2Cl_2 and separated by thin-layer-chromatography. The products are extracted with CH_2Cl_2 ; 1 and 2 are obtained as crystals, 3 and 4 as oils from dichloromethane solution.

Z-5-Benzylidene-1,3-dimethyl-4-thiohydantoin (1). TLC eluant cyclohexane/diethylether 1: 1, R_f 0.72. Yield 27%, m.p. 87–89°C. Anal. calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{OS}$: C 62.05, H 5.21, N 12.06. Found: C 62.05, H 5.21, N 11.96. ^1H -NMR (CDCl_3): Signals at 0.77 (t, 3H, CH_2CH_3), 1.31 (d, 6H, CH_3), 5.36 (m, 1H, C_6H_5), 7.27–7.44 (m, 5 + 1H, C_6H_5 , CH). ^{13}C -NMR (CDCl_3): Signals at 29.2 (CH_3), 31.9 (CH_3), 115.3 (C_6H_5), 127.7, 129.0 (o, m), 127.9 (p), 132.9 (i) (C_6H_5), 135.8 ($\text{CH}=\text{C}$), 155.7 ($\text{C}=\text{O}$), 188.6 ($\text{C}=\text{S}$). IR (KBr): Bands at 1737 vs ($\text{C}=\text{O}$), 1644 m ($\text{C}=\text{C}$), 1335 vs ($\text{C}=\text{S}$). M.S. (70 eV), m/e (M^+) 232.

Z-5-Benzylidene-1,3-diethyl-4-thiohydantoin (2). TLC eluant cyclohexane/diethylether 1: 1, R_f 0.79. Yield 21%, m.p. 41–43°C. $\text{C}_{14}\text{H}_{16}\text{N}_2\text{OS}$. ^1H -NMR (CDCl_3): Signals at 0.77 (t, 3H, CH_2CH_3), 1.31 (t, 3H, CH_2CH_3), 3.61 (q, 2H, CH_2CH_3), 4.06 (q, 2H, CH_2CH_3), 7.27–7.44 (m, 5 + 1H, C_6H_5 , CH). ^{13}C -NMR (CDCl_3): Signals at 12.2 (CH_2CH_3), 12.9 (CH_2CH_3), 37.6 (CH_2CH_3), 38.3 (CH_2CH_3), 116.3 (C_6H_5), 128.2, 129.1 (o, m), 128.5 (p), 133.7 (i) (C_6H_5), 135.0 ($\text{CH}=\text{C}$), 155.8 ($\text{C}=\text{O}$), 189.3 ($\text{C}=\text{S}$). IR (KBr): Bands at 1741 vs ($\text{C}=\text{O}$), 1643 m ($\text{C}=\text{C}$), 1278 s ($\text{C}=\text{S}$). M.S. (70 eV), m/e (M^+) 260.

Z-5-Benzylidene-1,3-dipropyl-4-thiohydantoin (3). TLC eluant cyclohexane/diethylether 7: 3, R_f 0.82. Yield 10%, oil. $\text{C}_{16}\text{H}_{20}\text{N}_2\text{OS}$. ^1H -NMR (CDCl_3): Signals at 0.47 (t, 3H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.97

(t, 3H, CH₂CH₂CH₃), 0.94–1.26 (m, 2H, CH₂CH₂CH₃), 1.58–1.91 (m, 2H, CH₂CH₂CH₃), 3.52 (t, 2H, CH₂CH₂CH₃), 3.95 (t, 2H, CH₂CH₂CH₃), 7.27–7.44 (m, 5 + 1H, C₆H₅, CH). ¹³C-NMR (CDCl₃): Signals at 10.4 (CH₂CH₂CH₃), 11.2 (CH₂CH₂CH₃), 20.3 (CH₂CH₂CH₃), 20.8 (CH₂CH₂CH₃), 43.9 (CH₂CH₂CH₃), 44.7 (CH₂CH₂CH₃), 116.4 (C₆H₅C), 128.1, 129.1 (o, m), 128.4 (p), 133.7 (i) (C₆H₅), 135.1 (CH=C), 156.2 (CO), 189.5 (CS). IR (film): Bands at 1748vs(C=O), 1641m(C=C), 1245s(C=S). M.S. (70 eV), m/e (M⁺) 288.

Z-5-Benzylidene-1,3-dibutyl-4-thiohydantoin (**4**). TLC eluant cyclohexane/diethylether 5: 1, *R_f* 0.76, Yield 8%, oil. C₁₈H₂₄N₂OS. ¹H-NMR (CDCl₃): Signals at 0.61 (t, 3H, CH₂CH₂CH₂CH₃), 0.96 (t, 3H, CH₂CH₂CH₂CH₃), 1.16–2.12 (m, 8H, CH₂CH₂CH₂CH₃), 3.54 (t, 2H, CH₂CH₂CH₂CH₃), 3.98 (t, 2H, CH₂CH₂CH₂CH₃), 7.19–7.45 (m, 5 + 1H, C₆H₅, CH). ¹³C-NMR (CDCl₃): Signals at 13.2 (CH₂CH₂CH₂CH₃), 13.6 (CH₂CH₂CH₂CH₃), 19.4 (CH₂CH₂CH₂CH₃), 20.0 (CH₂CH₂CH₂CH₃), 29.0 (CH₂CH₂CH₂CH₃), 29.5 (CH₂CH₂CH₂CH₃), 42.2 (CH₂CH₂CH₂CH₃), 43.1 (CH₂CH₂CH₂CH₃), 116.2 (C₆H₅C), 128.2, 129.2 (o, m), 128.4 (p), 133.9 (i) (C₆H₅), 135.3 (CH=C), 156.2 (CO), 189.5 (CS). IR (film): Bands at 1745vs(C=O), 1641m(C=C), 1256m(C=S). M.S. (70 eV), m/e (M⁺) 316.

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